

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Improved process and apparatus for the Treatment of Hydrocarbons

We, HYDROCARBON RESEARCH, INC., a Corporation of the State of New Jersey, United States of America, of 115, Broadway, New York 6, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to the high-temperature treatment of liquid hydrocarbons and is more particularly concerned with a process and apparatus for the efficient production of high octane gasoline from heavy oils, especially those which have a high content of sulfur, nitrogen or metal compounds.

15 Available cracking processes, which are effective in the treatment of ordinary heavy oil fractions, are of limited effectiveness in producing gasoline of commercially acceptable quality from low grade, heavy hydrocarbon oils, such as sour crudes, petroleum residues, shale oil, coal tar and the like, which have a high content of sulfur and/or nitrogen and/or metal compounds.

20 In general, this invention is particularly applicable to the conversion of heavy oil stocks which cannot be economically treated by conventional processes. It can be used on lighter oil stocks which contain catalyst poisons such as metals, and, therefore, are unsuitable for direct charging to catalytic crackers.

25 The present invention provides a process for the conversion of liquid hydrocarbons to lighter hydrocarbon fractions wherein the hydrocarbons contact a fluidized mass of solid particles in a primary cracking zone at an elevated conversion temperature and oxygen contacts said solid particles in a regeneration zone at a regeneration temperature higher than said conversion temperature to consume carbonaceous matter deposited on said solid particles by said hydrocarbons, including the steps of

passing said solid particles with absorbed hydrocarbons from the primary cracking zone 45 downwardly in a restrained fluidized state through a secondary cracking zone intervening between said primary cracking zone and said regenerating zone in counter-current contact with a hydrogen-containing gaseous stream initially at a temperature of at least 1600° F. thereby progressively increasing the temperature of said solid particles in their downward passage through said secondary cracking zone and effectively stripping 50 absorbed hydrocarbons from said solid particles, passing the stripped solid particles to said regenerating zone for regeneration by reacting residual carbon on said stripped solid particles at a temperature of at least 1600° F. with steam and oxygen whereby the resulting regeneration product gases contain a substantial proportion of hydrogen, carbon monoxide and steam, and flowing said regeneration product gases upwardly through said secondary cracking zone as said hydrogen-containing gaseous stream. 55 60 65

In a preferred embodiment of the invention, hydrocarbon oil is subjected to treatment at elevated temperatures in the presence of a particulate contact material or carrier and in a gaseous atmosphere produced by the reaction of carbon with oxygen and steam at temperatures above about 1600° F. and containing an amount of hydrogen which provides a hydrogen partial pressure of 35 to 200 psi. (pounds per square inch), preferably 75 to 150 psi., in the hydrocarbon treatment or reaction zone. The hydrocarbon oil, preferably preheated, is fed into the reaction zone (designated as the primary cracking zone) containing the comminuted solid carrier in fluidized condition. The primary cracking zone is superposed on and in communication with a higher temperature zone of restrained fluidization (hereinafter designated as the secondary cracking zone). 70 75 80 85

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Fluidization of the particulate carrier is restrained in the secondary cracking zone in the sense that the vertical movements of the fluidized particles are restricted to the extent that a temperature gradient is established along the vertical dimension of the secondary cracking zone, ranging from the temperature of the primary cracking zone which is contiguous with the upper end of the secondary cracking zone to the higher temperature of the carrier regeneration zone which is contiguous with the lower end of the secondary cracking zone. Such restrained fluidization is obtained by filling the secondary cracking zone with coarse packing bodies of the type of Raschig rings and Berl saddles.

In the primary cracking zone, a deposit of the heavier constituents of liquid hydrocarbon feed stock and carbon forms on the carrier particles and these particles are passed with restrained fluidization downwardly through the secondary cracking zone countercurrently to a gaseous stream containing steam and the gaseous products of reacting carbon with oxygen and steam at a temperature above about 1600° F., the gaseous stream thus contacting the carrier particles in intimate thin film relationship. From the secondary cracking zone, the particulate carrier passes into a subjacent regeneration zone wherein carbonaceous matter on the carrier is reacted with steam and oxygen at a temperature in the range of 1600 to 2500° F. to produce the previously mentioned gaseous atmosphere required in both the primary and the secondary cracking zones. Besides hydrogen, this gaseous atmosphere contains carbon monoxide, carbon dioxide and steam. The thus "regenerated" particulate carrier is then returned to the primary cracking zone. The regeneration product gases, after passing upwardly through the secondary cracking zone, enter the primary cracking zone to provide the atmosphere for the hydrocarbon conversion and are withdrawn together with the hydrocarbon conversion products from the top of the primary cracking zone.

From this gaseous effluent is recovered a high yield of high octane gasoline, even when the feed stock is a heavy crude or residual oil containing large quantities of sulfur, nitrogen and metal compounds. This high yield of high octane gasoline is obtained with minimum formation of gaseous hydrocarbons and with an effluent recovery of liquid hydrocarbons boiling above the gasoline range (i.e., boiling above 400° F.) which may be recycled to provide additional gasoline or utilized as feed for a catalytic cracker or sold as fuel.

In most cases, the gasoline produced by the process of this invention has a sulfur content within commercially desirable limits and is in other respects an acceptable product. In those cases where, because of the excessively poor quality of the oil treated, the gasoline produced although of much reduced sulfur content still

contains more sulfur than is desirable or has less than the desired stability characteristics, the sulfur content and the stability characteristics can be brought to more desirable values by known refining processes, e.g., catalytic treatment with hydrogen at elevated temperatures.

The particulate carrier which is employed in the process of the invention is any solid heat-resistant material which may be fluidized, such as sand, quartz, alumina, magnesia, zircon, beryl, bauxite or other like material, which will withstand the desired regeneration conditions including a temperature above 1600° F. without physically disintegrating or fusing.

The entire reaction system, i.e., the primary cracking zone, the secondary cracking zone and the regeneration zone, is maintained at a total pressure in the range of 150 to 800 psig. (pounds per square inch gage), preferably at 250 to 650 psig. Under these conditions, the desired hydrogen partial pressure of 35 to 200 psi., preferably 75 to 150 psi., is maintained in the primary and secondary cracking zones. A hydrogen partial pressure in excess of 200 psi. is not necessary since maximum benefits from the presence of hydrogen are obtained in the indicated range and there is little or no economic justification for employing a hydrogen partial pressure above 200 psi. The use of total pressures in the indicated range also provides a high oxygen partial pressure in the regeneration zone, increasing the rate of regeneration and consequently decreasing the height of this zone and that of the over-all system. The indicated range of total pressures also allows efficient recovery of the normally liquid hydrocarbon products from the primary cracking zone effluent.

In the primary cracking zone, the particulate carrier is maintained in freely fluidized condition; a superficial linear gas velocity of 0.25 to 2.5, preferably of 0.4 to 1.0, feet per second is generally provided in the primary cracking zone. The temperature of the primary cracking zone is maintained in the range of 850 to 1100° F., preferably in the range of 900 to 1050° F., by control of the temperature and quantity of carrier transferred from the regeneration zone, and by control of the temperature to which the hydrocarbon oil feed is preheated. The feed rate of hydrocarbon oil is desirably maintained at 0.2 to 3.0, preferably 0.5 to 1.5, volumes of liquid oil per hour per volume of the primary cracking zone. The oil partial pressure, determined essentially by the rate of hydrocarbon oil feed and the volume of regeneration gas, may vary from about 5 to 100 psi., preferably from 10 to 50 psi. It is a feature of the invention that the preferred range of temperature is higher and the preferred range of oil partial pressure lower than generally employed in thermal cracking processes, and as a consequence the gasoline which is produced is considerably higher in octane number than that produced in

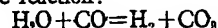
such processes, approximating 90 CFR octane number without use of tetra-ethyl lead or other anti-knock additives.

In the subjacent secondary cracking cracking zone, the particulate carrier is subjected to restrained fluidization by the presence of a fixed bed of packing bodies, e.g., 2-inch Raschig rings, so that the carrier particles are only permitted limited vertical and lateral movements while they continuously progress downwardly and are progressively heated by the upflowing regeneration product gases. Materials or devices of the type designated as "packing" or "trays", as are commonly utilized in fractionation, absorption or solvent extraction, are effective in providing the restrained fluidization of the solid carrier which is desired in the secondary cracking zone. The selected packing must withstand the reaction conditions in the secondary cracking zone. Obviously, undue restriction of the flow of the carrier through the secondary cracking zone would adversely affect the transfer of carrier particles from the primary cracking zone to the regeneration zone and thus interfere with the efficiency of the entire process. It has been found that the free horizontal area in the secondary cracking zone should for best results be 50 to 80% of the total horizontal area. This is particularly so when Raschig rings are employed.

As a consequence of the type of flow of particulate carrier which is obtained, a temperature gradient is established in the secondary cracking zone, with the top of this zone essentially at the temperature of the primary cracking zone and the bottom essentially at the temperature of the regeneration zone. It is a feature of the invention that heavy hydrocarbons which are not fully converted to volatile products in the primary cracking zone and remain as a deposit on the surfaces of the carrier particles pass downwardly with the carrier through the secondary cracking zone and there are converted at increasing temperatures in contact with the hot gases from the regeneration zone. Thus, there is achieved efficient conversion of heavy hydrocarbons into more volatile products which are desorbed from the particulate carrier and are carried upwardly into the primary cracking zone for further conversion and thence recovery of an increased yield of hydrocarbons in the gasoline range. Accordingly, not only is a minimum of the adsorbed heavy hydrocarbons permitted to form a carbonaceous deposit but also the carbonaceous deposit to be burned in the regeneration zone is relatively "dry", i.e., is relatively low in hydrogen content, so that the oxygen requirements of the process are materially reduced. The carbonaceous deposit on the carrier entering the regeneration zone usually amounts to about 5 to 15% by weight of the carrier.

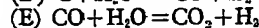
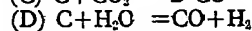
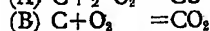
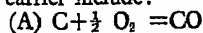
While it is not desired to be bound by any

particular theory of operation, experimental studies indicate that in the secondary cracking zone the steam and carbon monoxide present in the effluent from the regeneration zone undergo the reaction:—



As the temperature of the steam and carbon monoxide is decreased in passing upwardly through the secondary cracking zone, the equilibrium of the above reaction is shifted toward the right to evolve an ever increasing amount of nascent hydrogen. The nascent hydrogen thus generated comes into direct, intimate contact with the oil carried by the particulate carrier and minimizes the conversion of the oil to a carbonaceous residue even at relatively low hydrogen partial pressures. It has been determined that material benefits from the presence of nascent hydrogen are realized at a hydrogen partial pressure as low as 35 psi.

In the regeneration zone, the non-volatile carbonaceous deposit on the particulate carrier is reacted with regenerating gas consisting essentially of steam and oxygen, at a temperature of at least 1600 F., more particularly in the range of 1600 to 2500° F. and preferably in the range of 1700 to 2000° F. The regeneration of the carrier results in the production of a gaseous mixture comprising essentially hydrogen, carbon monoxide, carbon dioxide and excess steam. The principal reactions by which the carbonaceous deposit is removed from the carrier include:—



The regenerating gas contains a preponderance of steam and a minor proportion of high purity oxygen, the latter, more specifically containing at least about 90% by volume of oxygen, preferably at least 95% by volume of oxygen, and obtained, for example, by air liquefaction and rectification. The composition of the regenerating gas insures a maximum yield of hydrogen in accordance with the foregoing reactions. Steam-to-oxygen volume ratios in the range of 1.5:1 to 5:1 are generally satisfactory for generating the required quantity of hydrogen. It is preferable, as a practical matter, to employ a steam-to-oxygen volume ratio of the order of 2:1 to 3:1 and thereby avoid a very high regeneration temperature. As a general rule, it is advisable to conduct the regeneration at a temperature approaching the maximum permissible with the carrier and reactor materials employed, utilizing the smallest steam-to-oxygen volume ratio which will provide the desired temperature control.

The effluent gas mixture from the regeneration zone passes through the secondary and primary cracking zones, serving as the atmosphere for the hydrocarbon conversion reactions

and as the principal medium for carrier fluidization.

5 An up-transport zone serves to return hot regenerated carrier to the primary cracking zone. In the up-transport zone which is fed with carrier particles from the regeneration zone, the carrier particles flow upwardly because of the lower fluid-static head extant in this zone. The gas velocity in the up-transport zone is generally over 0.5 foot per second and not above 5 feet per second, depending to a great extent on the particle size and density of the comminuted carrier utilized as well as the gas velocities in the other zones. The gas velocity in the up-transport zone is preferably supplied by a stream of steam or, in some cases, by a stream of product gas from which all hydrocarbons containing more than two carbon atoms have been removed. In any case, the velocity employed is the lowest possible to obtain adequate circulation of carrier. The rate of circulation of the carrier is controlled to maintain the desired temperature in the primary cracking zone by regulation of the fluid-static heads in the various zones and/or by suitable valving between zones.

10 In another embodiment of the invention, there is provided a third cracking zone (hereinafter designated as the recycle cracking zone) which is in communication with and intermediate the primary and secondary cracking zones. In this embodiment, the recycle cracking zone is maintained at a temperature of at least 10° F. higher than that in the primary cracking zone; the temperature in the recycle cracking zone rarely exceeds 1450° F. The additional recycle cracking zone is employed when it is desirable to recycle liquid products of the process boiling above the gasoline range in order to increase the yield of gasoline. Since the liquid hydrocarbon oil fed to the recycle cracking zone is more refractory than that fed to the primary cracking zone, the former is operated at a higher temperature. With a recycle cracking zone, there is also provided a second up-transport zone, through which regenerated carrier is transported from the regeneration zone directly to the recycle cracking zone at a rate to obtain the desired temperature. Temperatures above 1250° F. are employed in the recycle cracking zone when it is desired to recycle to extinction liquid products boiling above the gasoline range so that the only recovered products of the process are gasoline and gas. This mode of operation, which permits the production of large amounts of gaseous fuel of high heating value when the demand for such fuel is greater than that for low grade Bunker C fuel, is a feature of the invention which is made possible by the high regeneration temperatures utilized in the process.

15 The hydrocarbon conversion products of the process are separated from the primary cracking zone effluent by the conventional

methods. The gasoline product, which has a clear research octane rating of about 90, may be further treated, as previously mentioned, to effect additional desulfurization and to improve gum stability, when desired. Higher boiling products, if not recycled to extinction, are conventionally utilized as furnace oils or may be catalytically cracked. The normally gaseous portion of the total effluent may be used as fuel or utilized in syntheses requiring hydrogen and carbon monoxide as reactants.

To describe and explain this invention more fully, reference is made to the accompanying drawings wherein:—

Figure 1 is a diagrammatic vertical section of a reactor embodying features of the invention and adapted for carrying out the above-described process; and

Figure 2 is a similar view of another reactor embodying features of the invention and particularly adapted for an operation involving the recycling of some of the liquid products.

The apparatus illustrated in Figure 1 comprises an upright cylindrical vessel 10 having opposed ends 12 and 14. In the lower portion of vessel 10 is disposed a concentric tubular shell 16 formed from a refractory insulating material such as fire brick, alundum or the like, the outer surface of shell 16 being spaced from the inner surface of vessel 10 to define an annular dead space therebetween which is filled with the particulate carrier used in vessel 10. The shell 16 holds the regeneration zone 18 and the secondary cracking zone 20, which are separated by a perforated plate or grid 22. Shell 16 protects the metal walls of vessel 10 from the high temperatures which are attained in the regeneration zone and the secondary cracking zone. Secondary cracking zone 20 is filled with packing 23 to give restrained fluidization of the carrier particles in zone 20. When the apparatus is in operation, it is filled with fluidized carrier to level 24 in primary cracking zone 26. The carrier is maintained in continuous circulation throughout vessel 10, moving downwardly from primary cracking zone 26 through secondary cracking zone 20 into regeneration zone 18 and thence returning to primary cracking zone 26. For the return of regenerated carrier there is provided an axial up-transport tube 28 extending upwardly from end 14 of vessel 10 through regeneration zone 18 and secondary cracking zone 20 with an outlet end 30 discharging into the bottom of primary cracking zone 26. Passage of regenerated carrier into up-transport tube 28 is effected by means of a valve arrangement comprising an inlet aperture 32 in the wall of up-transport tube 28 and a valve body 34 mounted on a tube 36 which is exteriorly adjusted by turning threaded handle 35 to move tube 36 and valve body 34 in a vertical direction. Depending on the position of valve body 34, the inlet aperture 32 may vary from completely open to completely

closed. Movement of the carrier upwardly through tube 28 is effected by supplying a stream of fluidizing gas through tube 36 into up-transport tube 28.

- 5 Steam and oxygen are introduced into regeneration zone 18 through an inlet conduit 38 provided with distributing means 40. The oil feed is in like manner introduced into primary cracking zone 26 through inlet conduit 42 provided with distributing perforations 44. The oil conversion products together with regeneration product gases are removed from vessel 10 through top outlet 46, a cyclone 48 being advantageously provided to remove at least some of the carrier which may be entrained in the effluent gases. The exterior of vessel 10 is, of course, suitably provided with insulation (not shown) to prevent undue heat loss.
- 10 Figure 2 shows a modified form of the apparatus of Figure 1 particularly suited for operation with continuous or intermittent recycle of high boiling hydrocarbons. The apparatus of Figure 2 comprises a vessel 110, a tubular shell 116 and inlet conduits 138 and 142. Packing 123 is supported on grid 122 and extends to a level substantially below the top of shell 116. The space between the top of packing 123 and the top of shell 116 forms recycle cracking zone 127 which is provided with recycle oil inlet conduit 131. There are two up-transport tubes 128 and 129, extending upwardly into primary cracking zone 126 and recycle cracking zone 127, respectively.
- 15 Since recycle cracking zone 127 is maintained at a higher temperature than that of primary cracking zone 126, the two fluidization zones are separated by flow-restricting means such as a grill, perforated plate or baffles. Figure 2 illustrates the flow-restricting means as a series of baffles 135. For a large temperature difference between zones 126 and 127, a shallow bed of packing bodies like Raschig rings may be supported on baffles 135. When the apparatus of Figure 2 is in operation, the total effluent is treated to separate high-boiling hydrocarbons which are recycled to the apparatus through inlet conduit 131.
- 20 The following Examples 1, 3 and 4 illustrate the invention more specifically without, however, being intended as limitative thereof. Example 2 is included as illustrative of a prior art process to show the improved results obtained by the process of the present invention:—

#### EXAMPLE 1

- Referring to Figure 1, vessel 10 is charged with bauxite of 0.0331 inch to 0.0017 inch particle size with 90% between 0.0166 inch to 0.0029 inch particle size and steam is introduced through pipe 36 to fluidize this carrier. The oil feed is supplied through inlet conduit 42 while oxygen of 95% by volume purity and steam are introduced through inlet conduit 38.

The oil feed is a 15% East Texas residuum having the following characteristics:—

Gravity, degrees API	-	-	-	14.0
Sulfur, wt. per cent	-	-	-	0.82
Carbon, Ramsbottom, wt. per cent	-	-	-	10.4

The total pressure in vessel 10 is maintained at 400 psig, with a hydrogen partial pressure of 75 psi. The oil feed is preheated to about 800° F. and fed into primary cracking zone 26 at the rate of 0.5 volume of oil per hour per volume of primary cracking zone. The temperature in primary cracking zone 26 is 980° F. and the temperature in regeneration zone 18 is 1750° F. The temperature at the top of secondary cracking zone 20 is slightly above the temperature of zone 26 and progressively increases through zone 20 until the temperature at the bottom of secondary cracking zone 20 is slightly below the temperature of zone 18. The volume ratio of steam to oxygen introduced through inlet conduit 38 is 2:1. During operation, the bauxite particles are in continuous circulation, passing from primary cracking zone 26 downwardly through secondary cracking zone 20 into regeneration zone 18 and thence being transported upwardly through up-transport tube 28 back to primary cracking zone 26. The flow of steam and oxygen through inlet conduit 38 and the flow of steam through tube 36 and the setting valve 34 are controlled to obtain the specified pressures and temperatures.

The effluent vapors are continuously removed through outlet 46 and condensed. The yields of the various products are set forth in the first column of Table 1 which follows. The gasoline fraction, i.e., the fraction ranging from C<sub>4</sub> hydrocarbons to a 400° F. end point, has a clear research octane number of 89 and a sulfur content of 0.1% of weight.

#### EXAMPLE 2

For purposes of comparison, a run is made not following the teaching this invention. This run is made in the apparatus of Figure 1 as used in Example 1 except that the Raschig ring packing 23 is removed. All of the operating conditions of Example 1 are repeated except that, in the absence of packing in the secondary cracking zone, the regeneration temperature does not rise above 1400° F. and heavy hydrocarbons carried by the bauxite leaving the primary cracking zone are not effectively converted into valuable hydrocarbon products in the secondary cracking zone. Thus, it is necessary to use twice as much oxygen as is used in Example 1. The conversion products of this example are shown in the second column of Table 1. The coke and gas yields are materially higher than those for Example 1 and the production of valuable liquid products is correspondingly reduced.

#### EXAMPLE 3

A West Texas-New Mexico residuum is pro-

cessed substantially as set forth in Example 1. The specific gravity, sulfur content and Ramsbottom carbon residue of this residuum are 7.5° API, 2.95% by weight and 20.2% by weight, respectively. The product yields are shown in the third column of Table 1. The gasoline contains 0.44% by weight of sulfur and has a 90 clear CFRR octane rating. It is noteworthy that the "coke" yield is only about 70% of the Ramsbottom carbon residue of the feed, whereas in conventional processes such as delayed coking, from which relatively low yields of relatively low octane rating gasoline are obtained, the coke yields are approximately 120% of the Ramsbottom carbon residue of the feed.

#### EXAMPLE 4

Boscan (Venezuela) crude is treated in apparatus as shown in Figure 2. This crude is extremely heavy (10.5° API gravity) and has high contents of sulfur (5.0% by weight), asphaltenic materials (13% by weights Ramsbottom carbon residue), and vanadium and other inorganic matter (ca. 0.3% by weight). When the apparatus of Figure 2 is operated with a primary cracking zone temperature of

985° F., a recycle cracking zone temperature of 1000° F. and a regeneration temperature of 1800° F., and by recycling hydrocarbons boiling in the range of 400 to 750° F. at the rate of 65 barrels per 100 barrels of crude fed to the primary cracking zone, the total recovered liquid yield corresponds to 79 barrels composed of 53 barrels of gasoline and 26 barrels of heavier hydrocarbons.

The regenerating gas consists of oxygen of 95% by volume purity and steam, the steam-to-oxygen volume ratio being 2.5:1. After recovering from the total effluent 79 barrels of liquid hydrocarbons per 100 barrels of charged crude, there remains a gas having the following approximate composition (volumes are given in millions of standard cubic feet):—

CH <sub>4</sub>	54.0	CO	69.5
C <sub>2</sub> H <sub>4</sub>	6.0	CO <sub>2</sub>	73.5
C <sub>2</sub> H <sub>6</sub>	13.0	H <sub>2</sub> O	167.0
C <sub>3</sub> H <sub>6</sub>	7.0	H <sub>2</sub> S	12.5
C <sub>3</sub> H <sub>8</sub>	8.0	NH <sub>3</sub>	1.5
H <sub>2</sub>	86.0	N <sub>2</sub>	4.0

The clear research octane number of the gasoline obtained in this recycle operation on Boscan crude exceeds 90.

TABLE 1

EXAMPLE		1	2	3
55	Charge stock	A*	A*	B*
	Gravity, °API - - - - -	14.0	14.0	7.5
	Operating temperatures, °F.			
	Primary cracking zone - - - - -	980	980	970
	Regeneration zone - - - - -	1750	1400	1750
60	Yields, % of charge			
	Gasoline (C <sub>1</sub> —400° F. e.p.), Vol. %	35.2	31.4	36.1
	Light gas oil (400—650° F.) Vol. %	28.5	28.7	28.3
	Heavy gas oil (650° F.+), Vol. %	23.6	15.5	21.4
	Gas (C <sub>1</sub> —C <sub>3</sub> ), Wt. % - - - - -	10.1	15.6	8.9
65	Coke **, Wt. % - - - - -	10.7	17.5	14.6

\*A=East Texas residuum

B=West Texas-New Mexico residuum

e.p.=end point

\*\*Calculated from the carbon monoxide and carbon dioxide in the product gas.

#### 70 WHAT WE CLAIM IS:—

1. A process for the conversion of liquid hydrocarbons to lighter hydrocarbon fractions wherein the hydrocarbons contact a fluidized mass of solid particles in a primary cracking zone at an elevated conversion temperature and oxygen contacts said solid particles in a regeneration zone at a regeneration temperature higher than said conversion temperature to consume carbonaceous matter deposited on said solid particles by said hydrocarbons, including the steps of passing said solid particles with absorbed hydrocarbons from the primary cracking zone downwardly in a restrained fluidized state through a secondary cracking zone intervening between said primary cracking zone and said regenerating zone in counter-current contact with a hydro-

gen-containing gaseous stream initially at a temperature of at least 1600° F. thereby progressively increasing the temperature of said solid particles in their downward passage through said secondary cracking zone and effectively stripping absorbed hydrocarbons from said solid particles, passing the stripped solid particles to said regenerating zone for regeneration by reacting residual carbon on said stripped solid particles at a temperature of at least 1600° F. with steam and oxygen whereby the resulting regeneration product gases contain a substantial proportion of hydrogen, carbon monoxide and steam, and flowing said regeneration product gases upwardly through said secondary cracking zone as said hydrogen-containing gaseous stream.

2. A process according to Claim 1, wherein the liquid hydrocarbon is a heavy oil to be converted to gasoline and a hydrogen-containing atmosphere is maintained in the cracking zones. 5
  3. A process according to Claim 1 or 2, wherein the said regeneration product gases are passed upwardly through said secondary and primary cracking zones to provide therein a hydrogen-containing atmosphere, and the regenerated solid particles of contact material are returned to said primary cracking zone from said regenerating zone. 10
  4. A process according to Claim 1, 2 or 3, wherein the temperature at the top of said secondary cracking zone is close to that of said primary cracking zone and increases downwardly through said secondary cracking zone to a temperature at the bottom of said secondary cracking zone close to that of the regeneration zone, the temperature in said regeneration zone being about 1600 to 2500° F. 15
  5. A process according to any one of the preceding claims, wherein an elevated operating pressure is maintained such that the hydrogen exerts a partial pressure of about 35 to 200 psi in the cracking zones. 20
  6. A process according to any one of the preceding claims, wherein the elevated temperature in the primary cracking zone is in the range of about 850 to 1100° F. 25
  7. A process according to any one of the preceding claims, wherein the hydrogen of the hydrogen-containing atmosphere in the cracking zones exerts a partial pressure in the range of about 75 to 150 psi. 30
  8. A process according to any one of the preceding claims, wherein the steam and oxygen used in regenerating the contact material are supplied in a steam-to-oxygen volume ratio in the range of about 1.5:1 to 5:1. 35
  9. A process according to any one of the preceding claims, wherein the operating pressure is in the range of 150 to 800 psig. 40
  10. A process according to any one of the preceding claims, wherein the operating pressure is in the range of 250 to 650 psig. 45
  11. A process according to any one of the preceding claims, wherein the atmosphere in the cracking zones contains steam. 50
  12. A process according to any one of the preceding claims, wherein gasoline hydrocarbons and higher-boiling hydrocarbons are separated from the resulting conversion products and at least a portion of said higher-boiling hydrocarbons are returned to a recycle cracking zone located between and contiguous to each of the primary and secondary cracking zones and containing said solid particles of contact material in a fluidized state and said hydrogen-containing atmosphere, maintaining said recycle cracking zone at a higher temperature than said elevated temperature in said primary cracking zone, passing said solid particles of contact material from said primary to said recycle cracking zone and then downwardly through the secondary cracking zone in a restrained fluidized state. 55
  13. A process according to Claim 12, wherein the elevated temperature in the primary cracking zone is in the range of 900 to 1050° F. and the higher temperature in said recycle cracking zone does not exceed 1450° F. 60
  14. Apparatus for carrying out the process according to any one of the preceding claims, comprising an upright elongated vessel, a bed of packing bodies disposed in an intermediate portion of said vessel, the top of said bed communicating with a hydrocarbon conversion zone in said vessel and the bottom of said bed communicating with a contact material regeneration zone in said vessel, an inlet for the introduction of regenerating gas into said regeneration zone, means for injecting a hydrocarbon oil into said conversion zone, an outlet for gaseous products at the top of said vessel, a conduit communicating at its lower end with said regeneration zone and at its upper end with said conversion zone, and means for injecting a transport gas into the lower end of said conduit to lift contact material from said regeneration zone to said conversion zone. 65
  15. Apparatus according to Claim 14, wherein a flow-restricting baffle structure extends horizontally across the conversion zone above the means for injecting a hydrocarbon oil, and a second means is provided for injecting a hydrocarbon oil into said vessel above said baffle structure. 70
  16. The process for the conversion of liquid hydrocarbons to lighter hydrocarbon fractions substantially as hereinbefore described. 75
  17. The apparatus for the conversion of liquid hydrocarbons to lighter hydrocarbon fractions substantially as described with reference to and as illustrated in Fig. 1 or Fig. 2 of the accompanying drawings. 80
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